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14. ABSTRACT

During this project period we focused predominantly on explicit-atom MD simulations and first principles DFT calculations. This involved the force field parameterization for new molecules, i.e., cyclopentene, and the exploration of various DFT codes to identify the one most suitable for our purpose. We conducted several proof of concept studies, concentrating on the structural developments in the immediate vicinity of the surface with which the polymer comes into contact. These studies include: Wetting behavior by non-reactive alkanes of various chain lengths, Deposition of alkane chains with reactive sulfur-bearing end groups, First-principles quantum mechanical calculations predicting density of reactive surface sites for functionalization with benzene molecules, Surface functionalization and co-polymerization of cyclopentene, and Simulations were carried out for (111) and (100) copper surfaces. The principal findings are summarized in the following.

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MOLECULAR MODELING OF INTERFACIAL BEHAVIOR OF NANOMATERIALS

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Executive Summary

This project was part of a US-Taiwan-Singapore research collaboration, and served to seed an effort in atomic scale simulations of the structure and properties of interfaces in polymer-matrix composites. The focus of this project was on new approaches to generate realistic interfacial structures by reproducing the transport and reaction processes that govern structural developments in the actual systems. To this end we combined several atomistic simulation techniques, including first-principles quantum mechanical calculations and reactive molecular dynamics simulations.

We successfully carried out proof-of-concept studies, including the deposition of non-reactive polymer chains, the grafting to the surface of linear alkane chains that carry a reactive end group, and the grafting from the surface combined with ring opening metathesis co-polymerization of cyclopentene. We also demonstrated the use of density functional theory calculations to identify the structure and energetics of surface functionalization as a function of the grafting density. These case studies clearly show that significantly different interfacial structures develop depending on the underlying process, thus confirming that the recreation of these processes in simulations is important for creating realistic structural models of interfaces.

In these preliminary studies, two scientific issues became apparent that warrant further investigation: (i) we find that the fraction of surface atoms that are in direct contact with polymer, either physicsorbed or chemically bonded, is generally less than 20% — a number that is unexpectedly low, and (ii) a thin layer of polymer that is absorbed onto develops a structure that is incompatible with the bulk polymer and therefore phase separates from it. As a result, a cleavage region develops between the two polymer phases that is more or less pronounced depending on the nature of the polymer and the process by which it is deposited onto the surface. Further investigation of these observations will be important in view of improving materials designs for polymer matrix nano-composites.

1. Introduction

The mechanical properties of polymer matrix composites reinforced by nano-sized particles are chiefly affected by phenomena in the interfacial regions between polymer and particles, which constitute a large volume fraction of such materials.[1-10] Furthermore, the intimate juxtaposition of phases with disparate mechanical characteristics at the nano-scale creates intricate geometries and a blend of properties that are no longer amenable to description by continuum mechanical formalisms. Predicting properties by extrapolation from the bulk behavior of individual phases is no longer reliable. To accurately understand elastic properties, plastic deformation, and fracture processes of polymer matrix nano-composites, it is essential to examine the governing interfacial interactions at the molecular level. To this effect, experimental methods of investigation provide only limited insight, and the lacking information must be acquired through atomic-scale simulations.

Pivotal for the accurate simulation-based prediction of interfacial properties is the ability to generate realistic models of interfacial structures in which all pertinent details can be clearly resolved. Invariably, the structures that develop at interfaces strongly depend on the governing phenomena, such as wetting, adhesion, chemical bonding, mechanical relaxation, as well as the thermal, mechanical, and chemical conditions under which these phenomena take place. Thus, to create reliable structural models we must reproduce the reaction and transport processes that underlie the formation of interfaces. Accurate representation of these processes require multi-scale simulation approaches, capable of accounting for details such as the electronic structure that determine the bonding strength between dissimilar materials and of describing the long-term relaxation behaviors that affect large spatial domains of the material.

2. Objectives

This project was designed to initiate work that ultimately leads to the ability of simulating the behavior of nano-particles embedded in a polymer matrix subject to deformation, including phenomena such as friction, impingement, slip, delamination, fracture, etc. The crucial initial step in achieving this goal is to establish the ability for generating realistic atomically resolved structural models of interfaces, particularly those involving dissimilar materials. This requires multi-scale simulation approaches, and developing the appropriate combination of computational methods has been the principal objective of this project. The central method for this investigation has been large-scale molecular dynamics (MD) simulations, based on a semi-empirical reactive force field that we have developed in our laboratory. The MD method has been complemented by first-principles quantum mechanical calculations to gain a more accurate description of atomic interactions across interfaces, and by coarse-grained particle dynamics (CGPD) simulations to accelerate the time evolution of the simulated structural developments. Specific milestones of this short-term project have been:

❖ First-principles calculations of small molecular groups bonded to a crystalline surface to establish bonding site densities

❖ Parameterization of our semi-empirical force field used in MD simulations based on the results of these quantum mechanical calculations.

❖ Large-scale MD studies comparing physisorption and reactive bonding of different polymeric species to validate our simulation approach and to gain basic insights into the development of interfacial structures in nano-composites.

3. Approach and Methodology

The challenge in generating realistic interfacial structures using simulations arises from the need to describe molecular interactions accurately and explicitly account for structural details, such as defects, at the atomistic level, while reproducing reaction and transport phenomena that take place on a time scale beyond the reach of elementary molecular simulations. Hence, to establish the ability of creating dependable structural models of interfaces in polymer matrix composites, we combined first-principles quantum mechanical calculations based on the density functional theory (DFT), large-scale MD simulations based on a reactive force field developed in our laboratory, and CGPD simulations, which we have pioneered during a previous project supported by AFOSR, and which we are continuing to develop as part of this research. A brief summary of the individual methodologies and the way they complement one another in the present context follows.

First principles calculations — The purpose of these calculations is to provide accurate descriptions of atomic interactions across interfaces, which constitutes a relatively uncharted territory in the case of boundaries between dissimilar materials. DFT methods directly yield bonding energies and forces between atoms. Furthermore, the results of DFT calculations can be used to optimize the parameters of semi-empirical interaction potentials used in large-scale MD simulations. DFT calculations, by virtue of including the electronic structure of bonding orbitals explicitly, provide the most reliable approach towards simulating atomic interactions.[11] For this project we used the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code.[12] This code uses the standard Kohn-Sham self-consistent density functional method in the local density (LDA-LSD) or generalized gradient (GGA) approximations, and norm-conserving pseudopotentials in its fully nonlocal (Kleinman-Bylander) form. The basis set is a very general and flexible linear combination of numerical atomic orbitals (LCAO). It allows arbitrary angular momenta, multiple-zeta, polarized and off-site orbitals. Electron wavefunctions and density are projected onto a real-space grid in order to calculate the Hartree and exchange-correlation potentials and their matrix elements. Besides the standard Rayleigh-Ritz eigenstate method, it allows the use of localized linear combinations of the occupied orbitals (valence-bond or Wannier-like functions), making the computer time and memory scale linearly with the number of atoms.

Reactive MD simulations — Since our goal is to generate realistic interfacial structures by reproducing the kinetic processes that underlie their formation, we must employ a dynamic simulation method capable of accommodating structural developments that entail significant changes in configuration and bonding structure. Our MD simulations will therefore be based on the reactive force field that we have developed in our lab for the simulation of inorganic and organic systems.[13-18] This potential includes several terms that take effect depending on the type of bonding that one attempts to describe, including three-body and dihedral angle terms to describe the directionality of bonds, Coulomb and dipolar interaction terms, dispersion terms, etc. Two features of this force field stand out. One is the ability to account for the redistribution of electron density upon formation or breaking of bonds, which is achieve through a charge transfer term. The other feature is that the angular constraints dynamically adjust when a change in the coordination number of an atom occurs. Both charge transfer and multiple-coordination aspects are particularly important when simulating systems that undergo reactions and significant structural reorganization, and that involve bonding between dissimilar materials, such as at interfaces. This potential was originally designed for the modeling of mixed covalent-ionic bonding and was successfully used to describe oxides in crystalline, glassy, and molten form. Meanwhile we have expanded the capabilities of our potential to model polymeric systems. In particular, we have successfully parameterized the force field for the study of polyhedral oligomeric silsesquioxanes (POSS) functionalized with various alkane polymeric chains,[16, 18-20] dicyclopentadiene,[21, 22] which is used as the self-healing agent in polymer matrix composites sub-

ject to cyclic loads and undergoes a Grubbs-catalyzed ring-opening metathesis polymerization to form highly cross-linked networks, and cyclopentene (this project).

Coarse-grained particle dynamics — Chemical reactions and structural relaxation in the systems of interest here are typically many orders of magnitude slower than the vibrational motion of atoms. Thus, since explicit-atom MD simulations cannot routinely accommodate the time scales characteristic of the structural evolution during the formation of interfaces, we further developed our CGPD simulation scheme.[22] Particles in CGPD represent groups of atoms, such as monomer molecules or nanometer-sized fragments of a chain-like or network structure. The motion of these particles is governed by simplified interaction potentials, designed to describe the diffusional rather than the vibrational motion of these particles. Reaction events are accounted for based on a set of rules derived from a combination of statistical formulations of rate processes and topological considerations. The question at the core of this approach is how to design the coarse-grained interaction potential so as to ensure a structural evolution of the system at this level that is compatible with the one that would result from an explicit atom simulation. To achieve the desired accuracy we are developing a targeted reverse mapping procedure, which at critical time intervals consists of reconfiguring strategically chosen portions of the coarse-grained structure with atomic resolution and relaxing the reverse-mapped structure as controlled by our reactive force field. Accordingly, MD and CGPD simulations will be tightly coupled.

4. Accomplishments

During this project period we focused predominantly on explicit-atom MD simulations and first principles DFT calculations. This involved the force field parameterization for new molecules, i.e., cyclopentene, and the exploration of various DFT codes to identify the one most suitable for our purpose. We conducted several proof of concept studies, concentrating on the structural developments in the immediate vicinity of the surface with which the polymer comes into contact. These studies include:

❖ Wetting behavior by non-reactive alkanes of various chain lengths

❖ Deposition of alkane chains with reactive sulfur-bearing end groups

❖ First-principles quantum mechanical calculations predicting density of reactive surface sites for functionalization with benzene molecules

❖ Surface functionalization and co-polymerization of cyclopentene

Simulations were carried out for (111) and (100) copper surfaces. The principal findings are summarized in the following.

4.1   Wetting Behavior

Before any adsorption or bonding of a polymer to a surface can occur, the polymer must come into contact with this surface, i.e., navigate its way to accessible sites on the surface to which it can become physisorbed or chemisorbed. On pristine surfaces, the extent of contact between polymer chains and the surface only depends on the structural compatibility between the two phases and the degree of flexibility and/or mobility of the polymer on the surface. Polymer chains that are already attached to the surface may hinder new ones from establishing adequate contact. As more polymer is deposited on the surface, fewer open sites remain available and the contact that can be established between new arrivals and the substrate becomes less energetically stable. The compounded effects of transport and relaxation processes that govern the dynamics of polymer chains while competing to settle into accessible surface sites determine the fraction of surface sites that are eventually occupied and the resulting interfacial structure.

To study this physisorption process and its controlling factors, we examined the role that the length of polymer chains has on the wetting behavior and the fraction of surface sites that become occupied at saturation. To this end we simulated the deposition of simple alkane chains C_nH_{n+2}, with n varying between 4 and 16. As the deposition surface we chose the Cu (111) plane. The surfaces measured 30x30 or 50x50 atoms. Metal atoms were arranged in a slab, about 6 atoms thick, and due to the periodic boundary conditions, the metal was surrounded on both sides by polymer and vice versa. The system contained between 500 and 2000 polymer chains.

In Fig. 1 the wetting behaviors of C_4H_{10} (top) and $C_{16}H_{34}$ are compared. The figure shows only the top layer of metal atoms and the layer of polymer chains immediately in contact with the metal are displayed. Bulk polymer is not shown in order to avoid obscuring the features of the surface layer. We can clearly discern the differences between the two systems. The short polyer chains deposit onto the surface sporadically, resulting in no particular order or pattern. Conversely, the longer chains tend to align by adapting to the periodicity of the metal surface, and form a pattern of small regular domains. In

Fig. 1 Top views of Cu (111) surfaces (blue atoms) wetted by C_4H_{10} (top) and $C_{16}H_{34}$ (bottom). Only polymer chains that make direct contact with the metal surface are shown.

the latter case, much better contact is established between polymer and metal surface. Polymer chains tend to adhere to the metal surface over their entire length. The overall energy of this surface layer is lowered by achieving both epitaxy with the metal lattice and order among polymer chains themselves over the spatial extent of each domain.

In fact, the packing efficiency in this physisorbed layer is so pronounced that is separates from the bulk liquid polymer, i.e., the structure of this layer, as influenced by that of the meatal surface, is significantly more ordered than that of the amoporhous bulk polymer. The gap between the physisorbed layer of polymer chains and the bulk of the polymer melt, which is indicative of this phase separation, is visually discernable in fig. 2. Superimposed is the 1-D carbon-carbon pair correlation function normal to the metal surface, revealing the same information quantitatively. While the bonding between metal surface and physisorbed polymer layer is due to relatively weak dispersive interactions, e.g., van der Walls forces, it is magnified by the regularity and high density of surface coverage. Hence, the weakest mechanical link in a polymer matrix composite in which polymer chains can order congruently with the surface structure of the embedded particles, is most likely between the physisorbed layer and the bulk polymer.

In future work we will compute the mechanical properties of these structures, and quantitatively establish the correlation length in surface patterning that provides maximum adhesion
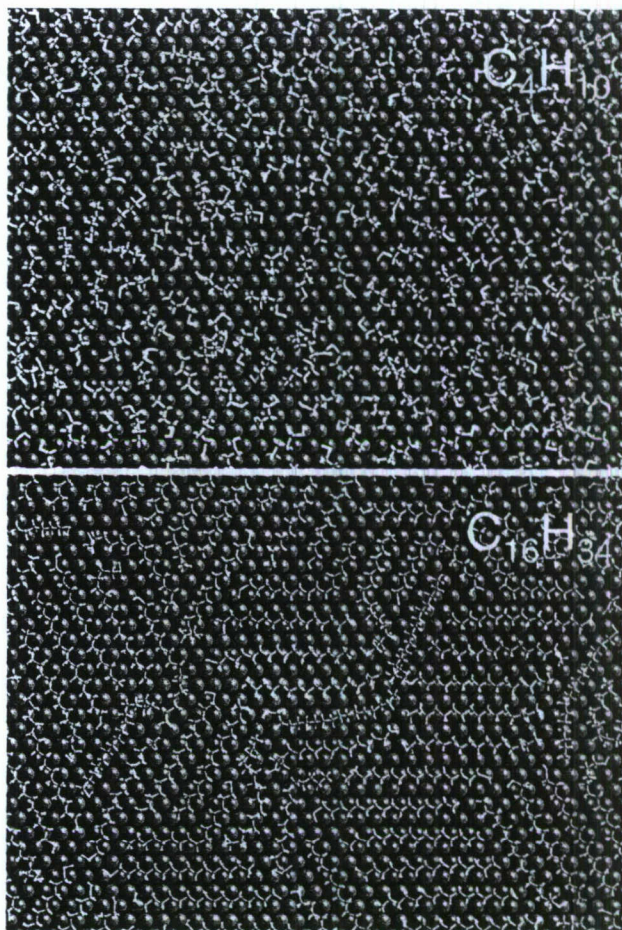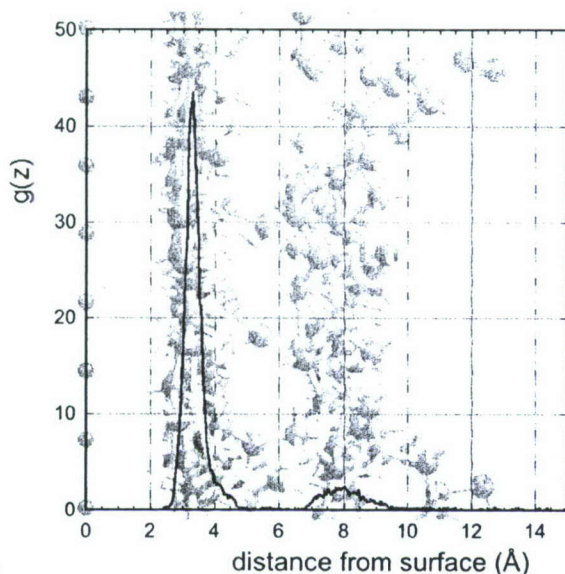
Fig. 2 Phase separation between the physisorbed layer of polymer chains and the bulk of the polymer melt. The gap between the two phases is visually discernable. Superimposed is the 1-D carbon-carbon pair correlation function normal to the metal surface, revealing the same information quantitatively.

strength. We expect to establish design criteria for the optimal degree of compatibility between surface structures and polymer characteristics.

4.2 Deposition of reactive groups

When studying the wetting behavior of alkane chains, we observed that the abiity of polymer to adhere flatly to the filler particle surface may induce a separation between a physisorbed layer and the bulk polymer, and cause a weakening of the entire composite structure. To reinforce this gap between layers, it may be desirable to orient some polymer chains perpendicular to the surface, so that they span across this gap. This can be accomplished by creating end groups in the polymer that are significantly more affine to the surface than the rest of the chain. Moreover, if these end groups can react, i.e., form chemical bonds with the surface atoms, much stronger adhesion can be expected.

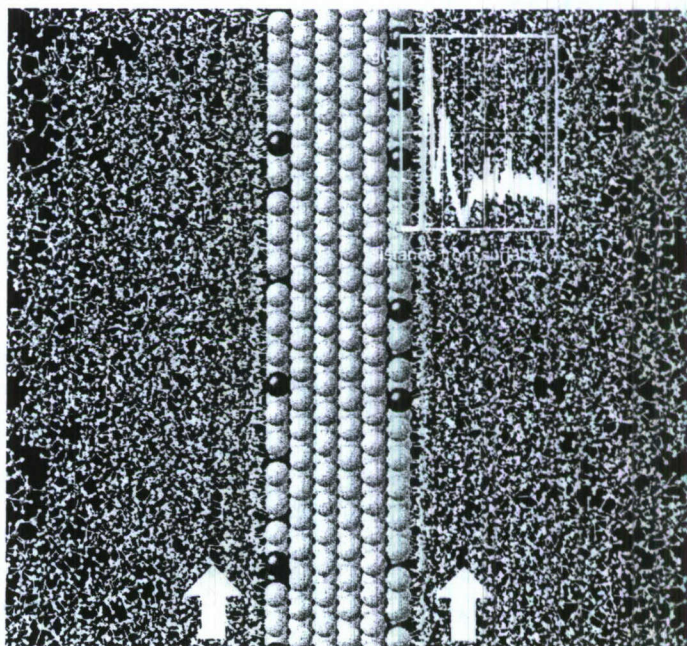There are principally two ways to bond polymer to a surface: one is grafting onto the surface and the other is grafting from the surface. In the former, the reactive group is carried by full-length polymer chains and must overcome steric hindrance to find its way to the surface. In the latter, the surface is first functionalized with small molecular groups that, after submersion into a solution of monomers, can participate in polymerization reactions resulting in the growth of long polymer chains, many of which having an endpoint bonded to the surface. We carried out simulation of both grafting approaches.

To model the first type of deposition we terminated alkane chains with a reactive sulfur group that can bond to the copper surface. Simulation ensembles were of similar size as described above. A necessary condition for grafting onto the surface is that the sulfur group comes in contact with open surface sites. Reactions then continue to occur until steric obstruction by the attached

Fig. 3 Deposition of C_4H_7S alkane chains functionalized on one end with a reactive sulfur group that can bond to the copper surface. Arrows indicate the gap separating the surface layer from the bulk polymer. Superimposed on the structure is the surface normal 1-D C-C pair correlation function.

chains prevents additional polymers from docking, and the fraction of bonded surface sites reaches a saturation level. Fig. 3 shows such an equilibrium configuration for the case of C_4H_7S. Polymer chains now attach in a head-on fashion, preventing the segments immediately following the sulfur group from lying down onto the surface. At a minimum the second carbon is maintained at a steady distance from the surface, as revealed by the second peak in the pair correlation function superimposed onto the structure. Nevertheless, also in the case of alkanes with reactive end groups, a dense polymer surface layer develops that is structurally incompatible with the bulk phase and therefore separates from it. The arrows in fig. 3 point to the low-density region that separates the two polymer phases. In the case of alkanes with reactive end-groups, however, the surface layer is thicker and the gap between surface and bulk phase is less pronounced; a larger number of alkane chains bridges it compared to the case of non-reactive chains.

Fig. 4 shows the fraction of occupied surface atoms at saturation as a function of the alkane chain length. As expected, this fraction decreases with increasing length, because the tails of longer chains provide more obstacles for new chains to arrive at the surface. This chain length dependence, however, seems to become less pronounced the longer the chains. Fig. 4 also shows the end-to-end distances of the grafted polymer chains, normalized with respect to the equilibrium extent of the corresponding linear chain. Accordingly, these chains are relatively straight, giving little cause for entanglement, and thus, providing little entropy-based mechanical rigidity.

4.3 Surface functionalization density

Developing reliable interaction potentials is crucial for the predictive capability of molecular simulations. One area that has been sorely neglected to date is potentials describing the interactions between dissimilar materials across interfaces. The most reliable

Fig. 4 Surface density (circles) and relative end-to-end distance (squares) of alkane chains grafted onto a Cu surface by means of a reactive end group, as a function of alkane chain length (open symbols). The solid symbols show results of co-polymerized cyclopentene for comparison.

computational approach to evaluate such interactions is first-principles quantum mechanical calculations. These methods are, however, impractical for the large configurations that we need to simulate in order to obtain representative structural models of interfaces. Thus, our strategy is to apply first-principles calculations to small structural segments and derive accurate parameterizations for empirical potentials.

To demonstrate this approach, we used DFT calculations to determine the ground state energies of pairs of benzene rings, doped with one reactive sulfur atom that bonds to copper, as a function of the spacing between them. Initially, we positioned these groups near Cu atoms at various distances from one another on a Cu (100) surface. These initial configurations were then allowed to relax and reach their minimum energy configurations. The results are shown in fig. 5. Fig. 5a shows the ground state energy as a function of the spacing between the anchors of the functional groups and fig. 5b the corresponding configurations. Accordingly, configuration (3) with anchor points about 5 Å apart, exhibits the lowest energy; functional groups that are placed closer together exhibit energies that are steeply increasing with decreasing distance and
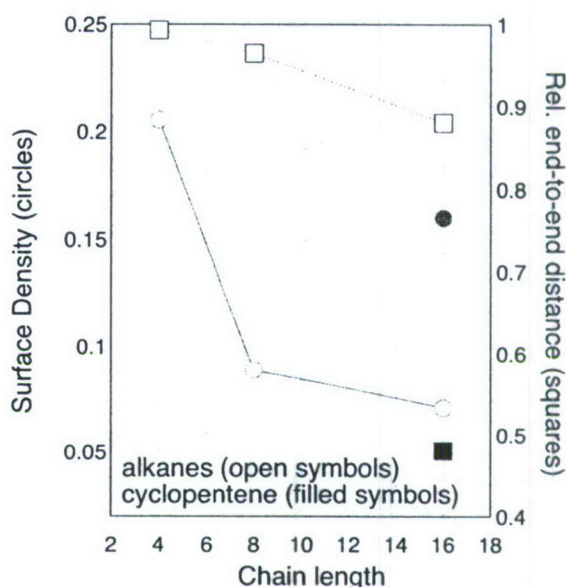
groups that are further apart asymptotically approach a plateau of constant energy reflecting the fact that these grafted molecules no longer interact with one another. Note that for configuration in which benzene groups are separated by 5 Å and larger, the benzene rings orient parallel to each other, whereas for configurations that are positioned closer together, they push away from each other, and the structures appear distorted. Interestingly, the appearance of this energy vs. distance curve is the same as that of an interaction potential. We therefore believe that this type of calculations can be used to determine potentials for both explicit atom MD and CGPD simulations. Currently, we have parameterized our reactive force field so that we achieve a surface packing density that is in agreement with these DFT calculations. A more judicious exploration of this approach will be undertaken in forthcoming research.
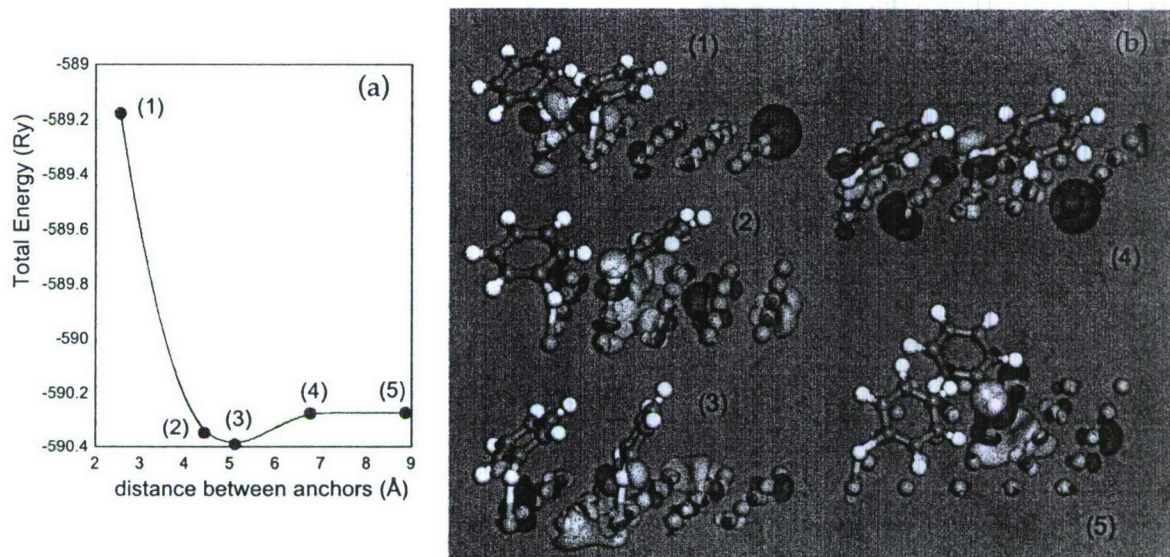

Fig. 5 (a) Ground state energy of benzene rings bonded to a Cu (100) surface via a sulfur intermediate, as a function of the distance between anchor points. (b) Molecular configurations corresponding to these ground state energies. The transparent envelopes represent iso-energy surfaces of the highest occupied molecular orbitals.

4.4 Co-polymerization with surface functional groups

As a case study of the grafting from the surface, we simulated the co-polymerization process of cyclopentene molecules. First, the space between surfaces was flooded with cyclopentene molecules carrying a reactive sulfur atom, similar to the benzene molecules described in the previous section. These are then allowed to react with surface Cu atoms upon coming in contact with them. Since these molecules have small spatial extent, the surface funcitonalization density that can be achieved is comparable to that of alkane molecules with about 5 or 6 members. Indeed, the solid circle in fig. 4 represents the density for this simulation. Note that the choice of a chain length of 16 is arbitrary since the carbon chains can continue to grow to almost 50 members (see fig. 6) for this same functionalization density. It is the end-to-end distance in fig. 4 that is to be attributed to the chain length of 16 (see below).

After the surface has been functionalized, the space between surfaces is filled with non-doped cyclopentene and a smaller number of dumbbell-shaped molecules representing a simplified version of Grubbs catalyst. Cyclopentene undergoes a ring opening metathesis polymerization (ROMP) similar to dicyclopentadiene (DCPD), which we had thoroughly studied during our preceding project, supported under the AFOSR MEANS initiative. Thus, we could apply knowledge acquired there in the present context. Fig. 6 shows that the ROMP process for cyclopentene follows first order reaction kinetics, i.e., the chain lengths increases at an exponen-

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tially decreasing rate and, for the system simulated here, reaches a length of almost 50 by the time the supply of monomer is exhausted.

The inset of fig. 6 depicts a representative configuration. In contrast to the alkane chain deposition, the polymer chains resulting from this ROMP co-polymerization are significantly more coiled up and entangled. This is evident from the average end-to-end distance shown in fig. 4 (solid square): it is less than half of the stretched-out length of the polymer. As with the alkane chains, a relatively dense surface layer, whose structure is distinct from the bulk polymer, also forms when the polymer is grown via co-polymerization. This is evident from the sharp first peak in the carbon-carbon pair correlation function (fig. 6b) Unlike with alkanes, however, in this case the surface and bulk phase are not separated by a distinct gap that creates an intrinsic mechanical weakness. Rather, there occurs a density drop delineating the edge of the layer, followed by a diffuse decay to the bulk density. Whether this is a consistent structural feature or a function of the degree of surface functionalization will be determined systematically in forthcoming research.
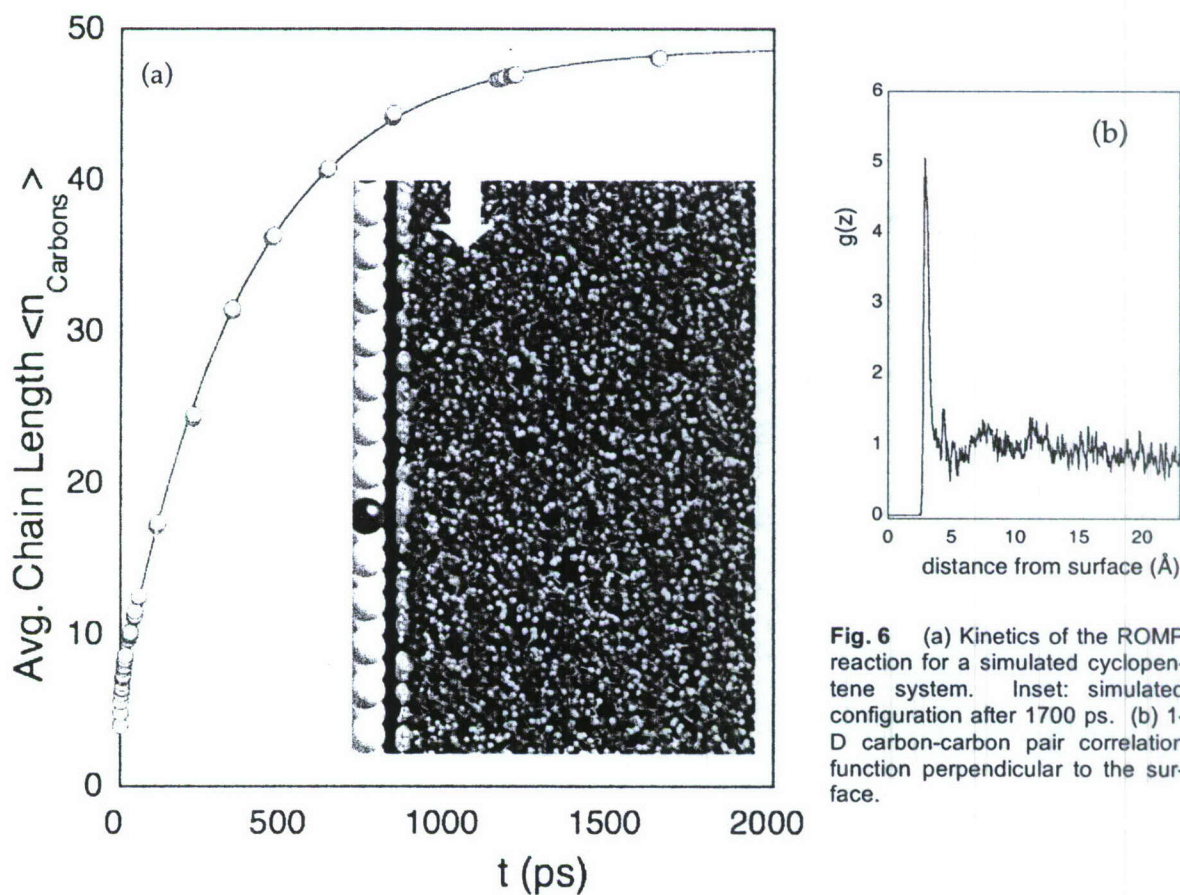

Fig. 6 (a) Kinetics of the ROMP reaction for a simulated cyclopentene system. Inset: simulated configuration after 1700 ps. (b) 1-D carbon-carbon pair correlation function perpendicular to the surface.

5. Summary and Outlook

A combination of first-principles DFT calculations and large-scale reactive MD simulations was used to generate structures of polymer-metal interfaces, by reproducing the reaction and transport phenomena that govern structural evolution. We successfully carried out proof-of-concept studies, including the deposition of non-reactive polymer chains, the grafting to the surface of linear alkane chains that carry a reactive end group, and the grafting from the surface combined

with ROMP co-polymerization of cyclopentene. We also demonstrated the use of DFT calculations to identify the structure and energetics of surface functionalization as a function of the grafting density. These case studies clearly show that significantly different interfacial structures develop depending on the underlying process, thus confirming that the recreation of these processes in simulations is important for creating realistic structural models of interfaces.

In these preliminary studies, two scientific issues became apparent that warrant further investigation: (i) we find that the fraction of surface atoms that are in direct contact with polymer, either physicsorbed or chemically bonded, is generally less than 20% — a number that is unexpectedly low, and (ii) a thin layer of polymer that is absorbed onto develops a structure that is incompatible with the bulk polymer and therefore phase separates from it. As a result, a cleavage region develops between the two polymer phases that is more or less pronounced depending on the nature of the polymer and the process by which it is deposited onto the surface. Further investigation of these observations will be important in view of improving materials designs for polymer matrix nano-composites.

Hence, future work will include:

❖ Systematic studies of wetting and adhesion of a range of materials systems, varying both the characteristics of the polymer and nature of the particle surfaces

❖ Investigating the effect of size mismatches between polymer matrix and nano-particles due to differences in the coefficient of thermal expansion (CTE) or displacive phase transformation in the embedded phase

❖ Direct calculation of mechanical properties of interfacial regions subject to elastic or plastic deformation, especially in case large contrast in elastic properties between phases

❖ Accounting for environmental factors such as the presence of impurities, moisture, or corrosive agents

❖ Examining phenomena that affect the self-assembly behavior of nano-particles, such as the extents of interfacial regions, surface energies, and particle impingement

❖ Refining our multi-scale simulation approach, especially with regard to the coarse-graining and reverse mapping scheme.

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7. Interactions/Transitions:

a. Participation

AFOSR Annual Grantee/Contractor's Meeting on "Mechanics of Multi-functional Materials and Microsystems," August 23-30, 2006, Seattle, WA. Poster presentation: "Molecular Modeling of Interfacial Behavior of Nanomaterials"

AFOSR Annual Grantee/Contractor's Meeting on "Mechanics of Multi-functional Materials and Microsystems," June 25 - 28, 2007, Monterey, CA. Oral presentation: "Molecular Modeling of Interfacial Behavior of Nanomaterials."

AFOSR Annual Grantee/Contractor's Meeting of the AFRL Advanced Composite Branch & AFOSR Polymer Matrix Composite Program, August 7-10, 2007, Kettering, OH. Oral presentation: "Molecular Modeling of Interfacial Behavior of Nano-Composites."

b. Transitions

This work constitutes a part of a US-Taiwan-Singapore research collaboration, and served to seed an effort in atomic scale simulations of the structure and properties of interfaces in polymer-matrix composites. A direct meeting between parties involved was not possible during this short project period, but is still a top priority in the context of forthcoming efforts.

New collaborations with Dr. Ajit Roy from the Air Force Research Laboratory at Wright Patterson Air Force Base and Prof. H. Thomas Hahn, University of California, Los Angeles, have been initiated as a direct consequence of this project.